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(54) **A POLYMER/CLAY NANOCOMPOSITE COMPRISING A FUNCTIONALIZED POLYMER OR
OLIGOMER AND A PROCESS FOR PREPARING SAME**

EIN POLYMER/TON NANOVERBUNDSTOFF ENTHALTEND EIN FUNKTIONALISIERTES
POLYMER ODER OLIGOMER SOWIE EIN VERFAHREN ZUR HERSTELLUNG DESSELBEN

NANOCOMPOSITE POLYMERE/ARGILE COMPORANT UN POLYMER OU UN OLIGOMERE
FONCTIONNALISE ET PROCEDE DE PRODUCTION

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Description

[0001] This application claims priority to provisional patent application Serial No. 60/111,323, filed December 7, 1998.

[0002] This invention relates generally to a nanocomposite comprising a matrix polymer, a functionalized polymer or oligomer and a clay material. This invention also relates to articles produced from the nanocomposite and processes for producing the nanocomposite.

[0003] There is much interest in layered, clay-based polymer nanocomposites because of the improved properties exhibited by the nanocomposites. It is desirable to maximize delamination of the platelet particles into individual platelets in order to maximize some property improvements, including barrier improvements, and to minimize deleterious effects on some properties including elongation-at-break. Ideally, the clay is exfoliated into particles with size less than about 100 nm in order to achieve clarity in the polymer that is comparable to the clay-free polymer. To date, the only polymer/clay nanocomposites that meet this expectation are prepared by incorporation of organically treated clays during synthesis of the polymer from monomer.

[0004] It is widely known, however, that the amount of clay that can be admixed in a polymer and still exhibit exfoliation of the layered clay is limited and some mechanical properties, such as elongation-at-break, are often reduced considerably upon the addition of the clay. Researchers recognized the value of inventing melt compounding processes that provide exfoliated polymer/platelet particle composites, namely more versatility of polymer choice and clay loading and the potential for cost savings. However, the melt compounding processes explored to date do not provide sufficient exfoliation of the platelet particles.

[0005] Polyesters such as poly(ethylene terephthalate) (PET) are widely used in bottles and containers which are used for carbonated beverages, fruit juices, and certain foods. Useful polyesters have high inherent viscosities (I.V.s) that allow polyesters to be formed into parisons and subsequently molded into containers. Because of the limited barrier properties with regard to oxygen and carbon dioxide, PET containers are not generally used for products requiring long shelf life. For example, oxygen transmission into PET bottles that contain beer, wine and certain food products causes these products to spoil. There have been attempts to improve the barrier properties of PET containers by use of multilayer structures comprising one or more barrier layers and one or more structural layers of PET. However, multilayer structures have not found wide use and are not suitable for use as a container for beer due to the high cost, the large thickness of the barrier layer required, and poor adhesion of the barrier layer with the structural layer.

[0006] There are examples in the literature of polymer/clay nanocomposites prepared from monomers and treated clays. For example, U.S. Patent 4,739,007 discloses the preparation of Nylon-6/clay nanocomposites from caprolactam and alkyl ammonium treated montmorillonite. U.S. Patent 4,889,885 describes the polymerization of various vinyl monomers such as methyl methacrylate and isoprene in the presence of sodium montmorillonite.

[0007] Some patents describe the blending of up to 60 weight percent of intercalated clay materials with a wide range of polymers including polyamides, polyesters, polyurethanes, polycarbonates, polyolefins, vinyl polymers, thermosetting resins. Such high loadings with modified clays are impractical and useless with most polymers because the melt viscosities of the blends increase so much that they cannot be molded.

[0008] WO 93/04117 discloses a wide range of polymers melt blended with up to 60 weight percent of dispersed platelet particles. WO 93/04118 discloses nanocomposite materials of a melt processable polymer and up to 60 weight percent of a clay that is intercalated with organic onium salts. The use of functionalized polymers in the melt blending operation is neither contemplated nor disclosed.

[0009] U.S. Patent 5,552,469 describes the preparation of intercalates derived from certain clays and water-soluble polymers such as polyvinyl pyrrolidone, polyvinyl alcohol, and polyacrylic acid. Although the specification describes a wide range of thermoplastic resins including polyesters and rubbers that can be used in blends with these intercalates, there are no examples teaching how to make such blends. The use of ammonium containing materials is specifically excluded; thus, the use of ammonium functionalized polymers is neither contemplated nor disclosed.

[0010] The use of a hydroxy functionalized polypropylene oligomer and an organoclay in the preparation of a polypropylene/clay nanocomposite is disclosed by A. Usuki, M. Kato, T. Kurauchi, *J. Appl. Polym. Sci. Letters*, **15**, 1481 (1996). The use of a maleic anhydride-modified polypropylene oligomer and a stearylammonium-intercalated clay in the preparation of a polypropylene/clay nanocomposite is disclosed by M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, and A. Okada, *Macromolecules*, **30**, 6333 (1997). The use of ammonium-functionalized polymers or oligomers is neither contemplated nor disclosed.

[0011] JP Kokai patent no. 9-176461 discloses polyester bottles wherein the polyester contains unmodified sodium montmorillonite. Incorporation of the clay into the polyester by melt compounding is disclosed; however, the use of functionalized polymer was neither contemplated nor disclosed.

[0012] The following references are of interest with regard to chemically modified organoclay materials: U.S. Patent Nos. 4,472,538; 4,546,126; 4,676,929; 4,739,007; 4,777,206; 4,810,734; 4,889,885; 4,894,411; 5,091,462; 5,102,948; 5,153,062; 5,164,440; 5,164,460; 5,248,720; 5,382,650; 5,385,776; 5,414,042; 5,552,469; WO Pat. Application Nos. 93/04117; 93/04118; 93/11190; 94/11430; 95/06090; 95/14733; D. J. Greenland, *J. Colloid Sci.* **18**, 647 (1963); Y.

Sugahara et al., J. Ceramic Society of Japan 100, 413 (1992); P. B. Massersmith et al., J. Polymer Sci.: Polymer Chem., 33, 1047 (1995); C. O. Sriakhi et al., J. Mater. Chem. 6, 103(1996).

[0013] This invention seeks to meet the need for a melt compounding process that provides polymer/clay nanocomposites with sufficient exfoliation for improved properties and clarity for commercial applications, including film, bottles, and containers. The polymer nanocomposite materials of this invention are useful for forming packages that have improved gas barrier properties. Containers made from these polymer composite materials are ideally suited for protecting consumable products, such as foodstuffs, soft drinks, and medicines. This invention also seeks to provide a cost-effective method for producing layers with sufficient oxygen barrier and clarity for wide spread applications as multilayer bottles and containers, including beer bottles.

[0014] According to the present invention there are provided nanocomposites, articles formed from nanocomposites and processes for forming composites as set forth in the claims hereinafter.

[0015] In the following description "functionalized" means having an onium group bonded thereto in the context of the present invention.

[0016] Additional advantages of the invention will be set forth in part in the detailed description, including the examples which follow, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory of preferred embodiments of the invention, and are not restrictive of the invention, as claimed.

Detailed Description of the Invention

[0017] The present invention may be understood more readily by reference to the following detailed description of the invention and the examples provided therein. It is to be understood that this invention is not limited to the specific components, articles, processes and/or conditions described, as these may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

Definitions

[0018] It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. For example, reference to an "article," "container" or "bottle" prepared from the nanocomposite and process of this invention is intended to include the processing of a plurality of articles, containers or bottles.

[0019] Whenever used in this specification, the terms set forth shall have the following meanings:

"Layered clay material," "layered clay," "layered material" or "clay material" shall mean any organic or inorganic material or mixtures thereof, such as a smectite clay mineral, which is in the form of a plurality of adjacent, bound layers. The layered clay comprises platelet particles and is typically swellable.

"Platelets," "platelet particles" or "particles" shall mean individual or aggregate unbound layers of the layered material. These layers may be in the form of individual platelet particles, ordered or disordered small aggregates of platelet particles (tactoids), and/or small aggregates of tactoids.

"Dispersion" or "dispersed" is a general term that refers to a variety of levels or degrees of separation of the platelet particles. The higher levels of dispersion include, but are not limited to "intercalated" and "exfoliated."

"Intercalated" or "intercalate" shall mean a layered clay material that includes treated or organically modified layered clay material having an increase in the interlayer spacing between adjacent platelets particles and/or tactoids. In the present invention, "intercalate" may refer to a concentrate of a clay material and a functionalized oligomer and/or polymer.

"Exfoliate" or "exfoliated" shall mean platelets dispersed mostly in an individual state throughout a carrier material, such as a matrix polymer. Typically, "exfoliated" is used to denote the highest degree of separation of platelet particles.

"Exfoliation" shall mean a process for forming an exfoliate from an intercalated or otherwise less dispersed state of separation.

"Nanocomposite(s)" or "nanocomposite composition(s)" shall mean a polymer or copolymer having dispersed therein a plurality of individual platelets obtained from a layered clay material.

5 "Matrix polymer," "bulk polymer" or "bulk matrix polymer" shall mean a thermoplastic or thermosetting polymer in which the clay material is dispersed to form a nanocomposite. In this invention, however, the platelet particles are predominantly exfoliated in the matrix polymer to form a nanocomposite.

10 [0020] This invention relates to a polymer/clay nanocomposite and to melt compounding processes for preparing a polymer/clay nanocomposite composition by combining a clay, a melt processible matrix polymer, and a functionalized oligomer or polymer.

15 [0021] More specifically, this invention relates to a polymer/clay nanocomposite or process to prepare a polymer/clay nanocomposite composition comprising an oligomer or polymer that contains an onium group, preferably an ammonium group. Without being bound by a particular theory, it is believed that the ammonium group on the oligomer or polymer provides a driving force for intercalation of the oligomer or polymer into the clay gallery, which disrupts the tactoid structure and swells the clay to permit intercalation by the bulk matrix polymer.

20 [0022] The prior art has defined the degree of separation of clay (platelet particles) based on peak intensity and basal spacing value, or lack of predominant basal spacing, as determined by X-ray analyses of polymer-platelet particle composites. Even though X-ray analysis alone often does not unambiguously predict whether the platelet particles are individually dispersed in the polymer, it can often allow quantification of the level of dispersion achieved. Basal spacing by X-ray diffraction indicates the separation distance of a platelet in a tactoid rather than single platelets. X-ray diffraction intensity (basal spacing peak height) may correlate to barrier in an article resulting from a nanocomposite including a clay material. For example, a low basal spacing peak height indicates few tactoids; therefore, the remainder must be either individual platelets or tactoids that are disordered.

25 [0023] Moreover, in polymer nanocomposites, X-ray analysis alone does not accurately predict either the dispersion of the platelet particles in the polymer or the resultant gas barrier improvement. TEM images of polymer-platelet composites show that platelet particles which are incorporated into at least one polymer exist in a variety of forms, including, but not limited to individual platelets (the exfoliated state), disordered agglomerates of platelets, well ordered or stacked aggregates of platelets (tactoids), swollen aggregates of stacked platelets (intercalated tactoids), and aggregates of tactoids.

30 [0024] Without being bound by any particular theory, it is believed that the degree of improved gas barrier (decreased permeability) depends upon the embodiment ratio of the resulting particle platelets and aggregates, the degree to which they are dispersed or uniformly distributed, and the degree to which they are ordered perpendicular to the flux of the permeant.

35 [0025] To obtain the improvements in gas permeability according to the present invention, it is preferable that the platelet particles representative of the bulk of the composite be exfoliated, and preferably be highly exfoliated, in the matrix polymer such that the majority, preferably at least 75 percent and perhaps as much as at least 90 percent or more of the platelet particles, be dispersed in the form of individual platelets and small aggregates having a thickness in the shortest dimension of less than 30 nm and preferably less than 10 nm, as estimated from TEM images. Polymer-platelet nanocomposites containing more individual platelets and fewer aggregates, ordered or disordered, are most preferred.

40 [0026] Significant levels of incomplete dispersion (i.e., the presence of large agglomerates and tactoids greater than -30 nm) not only lead to an exponential reduction in the potential barrier improvements attributable to the platelet particles, but also can lead to deleterious affects to other properties inherent to polymer resins such as strength, toughness, heat resistance, and processability.

45 [0027] Again, without being bound by a particular theory, it is believed that delamination of platelet particles upon melt processing or mixing with a polymer requires favorable free energy of mixing, which has contributions from the enthalpy of mixing and the entropy of mixing. Melt processing clay with polymers results in a negative entropy of mixing due to the reduced number of conformations, which are accessible to a polymer chain when it resides in the region between two layers of clay. It is believed that poor dispersion is obtained using melt-processible polyesters, for example, because the enthalpy of mixing is not sufficient to overcome the negative entropy of mixing. In contrast, generally good dispersions are obtained with polyamides due to their hydrogen bonding character. However, the extent of this dispersion is frequently lessened because of the negative entropy of mixing.

50 [0028] Regarding the present invention, it has been found that processing a matrix polymer, a functionalized oligomer or polymer and a layered clay material gives a good dispersion of platelet particles in a resulting polymer nanocomposite, creating mostly individual platelet particles. The resulting nanocomposite has improved barrier to gas when formed into a wall or article compared to a neat polymer formed into the same or similar structure.

Polymers

[0029] Any melt-processible polymer or oligomer may be used in this invention. Illustrative of melt-processible polymers are polyesters, polyetheresters, polyamides, polyesteramides, polyurethanes, polyimides, polyetherimides, 5 polyureas, polyamideimides, polyphenyleneoxides, phenoxy resins, epoxy resins, polyolefins, polyacrylates, polystyrenes, polyethylene-co-vinyl alcohols (EVOH),

or their combinations and blends. Although the preferred polymers are linear or nearly linear, polymers with other architectures, including branched, star, cross-linked and dendritic structures may be used if desired.

[0030] The preferred polymers include those materials that are suitable for use in the formation of monolayer and/or 10 multilayer structures with polyesters, and include polyesters, polyamides, polyethylene-co-vinyl alcohols (such as EVOH), and similar or related polymers and/or copolymers. The preferred polyester is poly(ethylene terephthalate) (PET), or a copolymer thereof. The preferred polyamide is poly(*m*-xylylene adipamide) or a copolymer thereof.

[0031] Suitable polyesters include at least one dibasic acid and at least one glycol. A polyester of this invention may 15 comprise the polycondensation polymerization reaction product (or residue) of the glycol component and the dicarboxylic acid component. "Residue," when used in reference to the components of the polyester of this invention, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme, or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species.

[0032] The primary dibasic acids are terephthalic, isophthalic, naphthalenedicarboxylic, 1,4-cyclohexanedicarboxylic acid. The various isomers of naphthalenedicarboxylic acid or mixtures of isomers may be used, but the 1,4-, 1,5, 2,6-, 20 and 2,7-isomers are preferred. The 1,4-cyclohexanedicarboxylic acid may be in the form of cis, trans, or cis/trans mixtures. In addition to the acid forms, the lower alkyl esters or acid chlorides may also be used.

[0033] A polyester of this invention may be prepared from one or more of the following dicarboxylic acids and one or more of the following glycols.

[0034] The dicarboxylic acid component of the polyester may optionally be modified with up to 50 mole percent of 25 one or more different dicarboxylic acids. Such additional dicarboxylic acids include dicarboxylic acids having from 6 to about 40 carbon atoms, and more preferably dicarboxylic acids selected from aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of suitable dicarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, phenylenedi(oxyacetic acid), succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid.

Polyesters may also be prepared from two or more of the above dicarboxylic acids.

[0035] Typical glycols used in the polyester include those containing from two to ten carbon atoms. Preferred glycols 35 include ethylene glycol, propanediol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, diethylene glycol

The glycol component may optionally be modified with up to 50 mole percent, preferably up to 25 mole percent, and more preferably up to 15 mole percent of one or more different diols. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols include: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-di-40 ol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(2-hydroxyethoxy)-benzene, 2,2b-is-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane. Polyesters may also be prepared from two or more of the above diols.

[0036] Small amounts of multifunctional polyols such as trimethylolpropane, pentaerythritol, glycerol may be used, 45 if desired. When using 1,4-cyclohexanedimethanol, it may be the cis, trans or cis/trans mixtures. When using phenylenedi(oxyacetic acid), it may be used as 1,2; 1,3; 1,4 isomers. or mixtures thereof.

[0037] The polymer may also contain small amounts of trifunctional or tetrafunctional comonomers to provide controlled branching in the polymers. Such comonomers include trimellitic anhydride, trimethylolpropane, pyromellitic di-anhydride, pentaerythritol, trimellitic acid, pyromellitic acid and other polyester forming polyacids or polyols generally known in the art.

[0038] The polyesters of the present invention exhibit an I.V. of 0.25 to 1.5 dL/g, preferably 0.4 to 1.2 dL/g, and more 50 preferably of 0.7 to 0.9 dL/g. The I.V. is measured at 25°C in a 60/40 by weight mixture in phenol/tetrachloroethane at a concentration of 0.5 grams per 100 ml. Polyesters having an I.V. within the ranges specified above are of sufficiently high molecular weight to be used in the formation of the articles of the present invention.

[0039] Suitable polyamides include partially aromatic polyamides, aliphatic polyamides, wholly aromatic polyamides and/or mixtures thereof. By "partially aromatic polyamide," it is meant that the amide linkage of the partially aromatic polyamide contains at least one aromatic ring and a nonaromatic species. Suitable polyamides have an article forming molecular weight and preferably an I.V. of greater than 0.4.

[0040] Preferred wholly aromatic polyamides comprise in the molecule chain at least 70 mole% of structural units derived from *m*-xylylene diamine or a xylylene diamine mixture comprising *m*-xylylene diamine and up to 30% of *p*-xylylene diamine and an aliphatic dicarboxylic acid having 6 to 10 carbon atoms, which are further described in Japanese Patent Publications No. 1156/75, No. 5751/75, No. 5735/75 and No. 10196/75 and Japanese Patent Application Laid-Open Specification No. 29697/75.

[0041] Polyamides formed from isophthalic acid, terephthalic acid, cyclohexanedicarboxylic acid, *meta*- or *para*-xylylene diamine, 1,3- or 1,4-cyclohexane(bis)methylamine, aliphatic diacids with 6 to 12 carbon atoms, aliphatic amino acids or lactams with 6 to 12 carbon atoms, aliphatic diamines with 4 to 12 carbon atoms, and other generally known polyamide forming diacids and diamines can be used. The low molecular weight polyamides may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, pyromellitic dianhydride, or other polyamide forming polyacids and polyamines known in the art.

[0042] Preferred partially aromatic polyamides include, but are not limited to poly(*m*-xylylene adipamide), poly(*m*-xylylene adipamide-*co*-isophthalamide), poly(hexamethylene isophthalamide), poly(hexamethylene isophthalamide-*co*-terephthalamide), poly(hexamethylene adipamide-*co*-isophthalamide), poly(hexamethylene adipamide-*co*-terephthalamide), poly(hexamethylene isophthalamide-*co*-terephthalamide) or mixtures thereof. More preferred partially aromatic polyamides include, but are not limited to poly(*m*-xylylene adipamide), poly(hexamethylene isophthalamide-*co*-terephthalamide), poly(*m*-xylylene adipamide-*co*-isophthalamide), and/or mixtures thereof. The most preferred partially aromatic polyamide is poly(*m*-xylylene adipamide).

[0043] Preferred aliphatic polyamides include, but are not limited to poly(hexamethylene adipamide) and poly(caprolactam). The most preferred aliphatic polyamide is poly(hexamethylene adipamide). Partially aromatic polyamides are preferred over the aliphatic polyamides where good thermal properties are crucial.

[0044] Preferred aliphatic polyamides include, but are not limited to polycapramide (nylon 6), poly-aminoheptanoic acid (nylon 7), poly-aminonanoic acid (nylon 9), polyundecane-amide (nylon 11), polyaurylactam (nylon 12), poly(ethylene-adipamide) (nylon 2,6), poly(tetramethylene-adipamide) (nylon 4,6), poly(hexamethylene-adipamide) (nylon 6,6), poly(hexamethylene-sebacamide) (nylon 6,10), poly(hexamethylene-dodecamide) (nylon 6,12), poly(octamethylene-adipamide) (nylon 8,6), poly(decamethylene-adipamide) (nylon 10,6), poly(dodecamethylene-adipamide) (nylon 12,6) and poly(dodecamethylene-sebacamide) (nylon 12,8).

[0045] The most preferred polyamides include poly(*m*-xylylene adipamide), polycapramide (nylon 6) and poly(hexamethylene-adipamide) (nylon 6,6). Poly(*m*-xylylene adipamide) is a preferred polyamide due to its availability, high barrier, and processability.

[0046] The polyamides are generally prepared by processes which are well known in the art.

[0047] A polyamide of the present invention may comprise the polycondensation polymerization reaction product (or residue) of a diamine component and a dicarboxylic acid component, and/or those prepared by ring opening polymerization of lactams. "Residuc," when used in reference to the components of the polyamide of this invention, refers to the moiety that is the resulting product of the chemical species in a particular reaction scheme, or subsequent formulation or chemical product, regardless of whether the moiety is actually obtained from the chemical species.

[0048] The polyamides of the present invention exhibit an I.V. of 0.25 to 1.5 dL/g, preferably 0.4 to 1.2 dL/g, and more preferably of 0.7 to 1.0 dL/g. The I.V. is measured at 25°C in a 60/40 by weight mixture in phenol/tetrachloroethane at a concentration of 0.5 grams per 100 ml. Polyamides having an I.V. within the ranges specified above are of sufficiently high molecular weight to be used in the formation of the articles of the present invention.

[0049] The nanocomposite of the present invention also comprises a functionalized oligomer or polymer. By "functionalized", what is meant is that the oligomer or polymer preferably contains a functional group that provides for increased intercalation of a clay material. Preferably, the functional group of the functionalized oligomer or polymer is an onium group, more preferably an ammonium group. It is preferred, but not required, that the onium group be positioned at or near the chain end of the polymer or oligomer. As stated above and without being bound by a particular theory, it is believed that the onium group on the oligomer or polymer provides a driving force for intercalation of the oligomer or polymer into the clay gallery, which disrupts the tactoid structure and swells the clay to permit intercalation by the bulk matrix polymer.

[0050] Although any functionalized oligomer or polymer is contemplated by this invention, preferred functionalized oligomers and polymers include, but are not limited to oligomeric or polymeric polyesters such as polycaprolactone, beta-butryrolactone, poly(ethylene adipate), poly(ethylene terephthalate), poly(ethylene naphthalate) and/or their copolymers; oligomeric or polymeric polyamides such as nylon-6, nylon-6,6, nylon-6,12, poly(*m*-xylylene adipamide) and/or their copolymers; oligomeric or polymeric polyolefins such as polystyrene, polyethylene, polypropylene, polybutadiene, polyisoprene, poly vinyl alcohol, poly vinyl acetate and/or their copolymers; oligomeric or polymeric polysiloxanes such as polydimethyl siloxane; and oligomeric or polymeric polyacrylates such as poly(methyl methacrylate), poly(2-ethylhexyl acrylate), poly(butyl acrylate) and/or their copolymers. More preferred are the oligomeric or polymeric polyesters, polyamide and polyolefins with the most preferred functionalized oligomers or polymers being polycaprolactone, poly(ethylene terephthalate), poly(*m*-xylylene adipamide), polystyrene, and/or polypropylene.

[0051] The I.V. of a functionalized oligomeric polyester prior to melt mixing is preferably from 0.05 and 0.5 dL/g, and more preferably from 0.1 dL/g to 0.3 dL/g as measured in a mixture of 60 weight percent phenol and 40 weight percent 1,1,2,2-tetrachloroethane at a concentration of 0.5 g/100ml (solvent) at 25°C. Moreover, the oligomeric polyester has a number average molecular weight of from 200 to 30,000 g/mol, more preferably 200 to 12,000 g/mol, and may be a homo or cooligomer.

[0052] The I.V. of a functionalized oligomeric polyamide prior to melt mixing is preferably from 0.1 and 0.5 dL/g, and more preferably from 0.3 dL/g to 0.5 dL/g as measured in a mixture of 60 weight percent phenol and 40 weight percent 1,1,2,2-tetrachloroethane at a concentration of 0.5 g/100ml (solvent) at 25°C. Moreover, the oligomeric polyamide has a number average molecular weight of from 200 to 30,000 g/mol, more preferably 200 to 12,000 g/mol, and may be a homo or cooligomer.

[0053] It is preferred, but not required, that a ammonium-functionalized polymer or oligomer have a number average molecular weight or inherent viscosity that is less than that of the matrix polymer. The ammonium-functionalized polymer or oligomer may comprise the same or different repeating units as that of the matrix polymer, provided that the ammonium-functionalized polymer or oligomer is sufficiently compatible with the matrix polymer to permit attainment of the desired properties. One or more ammonium groups may be present on the ammonium-functionalized polymer or oligomer. It is preferred, but not required, that the ammonium group be positioned at or near the chain end of the polymer or oligomer.

[0054] Although not necessarily preferred, the oligomers and/or polymers of the present invention may also include suitable additives normally used in polymers. Such additives may be employed in conventional amounts and may be added directly to the reaction forming the functionalized polymer or oligomer or to the matrix polymer. Illustrative of such additives known in the art are colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, reheat aids, crystallization aids, acetaldehyde reducing compounds, recycling release aids, oxygen scavengers, plasticizers, nucleators, mold release agents, compatibilizers, or their combinations.

[0055] All of these additives and many others and their use are known in the art and do not require extensive discussion. Therefore, only a limited number will be referred to, it being understood that any of these compounds can be used in any combination so long as they do not hinder the present invention from accomplishing its objects.

Clay Materials (Platelet Particles)

[0056] The nanocomposite composition of the present invention comprises less than 25 weight percent, preferably from 0.5 to 20 weight percent, more preferably from 0.5 to 15 weight percent, and most preferably from 0.5 to 10 weight percent of layered clay material. The layered clay material comprises platelet particles. The amount of platelet particles is determined by measuring the amount of silicate residue in the ash of the polymer/platelet composition when treated in accordance with ASTM D5630-94.

[0057] Useful clay materials include natural, synthetic, and modified phyllosilicates. Natural clays include smectite clays, such as montmorillonite, saponite, hectorite, mica, vermiculite, bentonite, nontronite, beidellite, volkonskoite, magadite, kenyata . Synthetic clays include synthetic mica, synthetic saponite, synthetic hectorite . Modified clays include fluorinated montmorillonite, fluorinated mica. Suitable clays are available from various companies including Nanocor, Inc., Southern Clay Products, Kunimine Industries, Ltd., and Rheox.

[0058] Generally, the layered clay materials useful in this invention are an agglomeration of individual platelet particles that are closely stacked together like cards, in domains called tactoids. The individual platelet particles of the clays preferably have thickness of less than 2 nm and diameter in the range of 10 to 3000 nm.

[0059] Preferably, the clays are dispersed in the polymer(s) so that most of the clay material exists as individual platelet particles, small tactoids, and small aggregates of tactoids. Preferably, a majority of the tactoids and aggregates in the polymer/clay nanocomposites of the present invention will have thickness in its smallest dimension of less than 20 nm. Polymer/clay nanocomposite compositions with the higher concentration of individual platelet particles and fewer tactoids or aggregates are preferred.

[0060] Moreover, the layered clay materials are typically swellable free flowing powders having a cation exchange capacity from 0.3 to 3.0 milliequivalents per gram of mineral (meq/g), preferably from 0.90 to 1.5 meq/g, and more preferably from 0.95 to 1.25 meq/g. The clay may have a wide variety of exchangeable cations present in the galleries between the layers of the clay, including, but not limited to cations comprising the alkaline metals (group IA), the alkaline earth metals (group IIA), and their mixtures. The most preferred cation is sodium; however, any cation or combination of cations may be used provided that most of the cations may be exchanged for organic cations (onium ions). The exchange may occur by treating a individual clay or a mixture of clays with organic cations.

[0061] Preferred clay materials are phyllosilicates of the 2:1 type having a cation exchange capacity of 0.5 to 2.0 meq/g. The most preferred clay materials are smectite clay minerals, particularly bentonite or montmorillonite, more particularly Wyoming-type sodium montmorillonite or Wyoming-type sodium bentonite having a cation exchange capacity from 0.95 to 1.25 meq/g.

[0062] Other non-clay materials having the above-described ion-exchange capacity and size, such as chalcogens, may also be used as a source of platelet particles under the present invention. Chalcogens are salts of a heavy metal and group VIA (O, S, Se, and Te). These materials are known in the art and do not need to be described in detail here.

[0063] Improvements in gas barrier result from increases in the concentration of platelet particles in the polymer. While amounts of platelet particles as low as 0.01 percent provide improved barrier (especially when well dispersed and ordered), compositions having at least 0.5 weight percent of the platelet particles are preferred because they display the desired improvements in gas permeability.

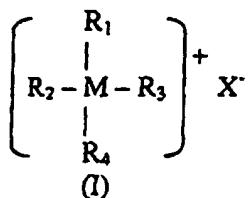
[0064] Prior to incorporation into the oligomer(s) or polymer(s), the particle size of the clay material is reduced in size by methods known in the art, including, but not limited to, grinding, pulverizing, hammer milling, jet milling, and their combinations. It is preferred that the average particle size be reduced to less than 100 micron in diameter, more preferably less than 50 micron in diameter, and most preferably less than 20 micron in diameter.

[0065] The clay material of this invention may comprise refined but unmodified clays, modified clays or mixtures of modified and unmodified clays. Generally, it is desirable to treat the selected clay material to facilitate separation of the agglomerates of platelet particles to individual platelet particles and small tactoids. Separating the platelet particles prior to incorporation into the polymer also improves the polymer/platelet interface. Any treatment that achieves the above goals may be used. Many clay treatments used to modify the clay for the purpose of improving dispersion of clay materials are known and may be used in the practice of this invention. The clay treatments may be conducted prior to, during, or after mixing the clay material with the polymer.

20 *Organic Cations*

[0066] In an embodiment of this invention, a modified or treated layered clay material is prepared by the reaction of a swellable layered clay with an organic cation (to effect partial or complete cation exchange), preferably an ammonium compound. If desired, two or more organic cations may be used to treat the clay. Moreover, mixtures of organic cations may also be used to prepare a treated layered clay material. The process to prepare the organoclays (modified or treated clays) may be conducted in a batch, semi-batch, or continuous manner.

[0067] Organic cations used to modify a clay material or a mixture of clay materials of a nanocomposite of this invention are derived from organic cation salts, preferably onium salt compounds. Organic cation salts useful for the nanocomposite and process of this invention may generally be represented by the following formula (I):



40 wherein M is either nitrogen or phosphorous; X⁻ is a halide, hydroxide, or acetate anion, preferably chloride and bromide; and R₁, R₂, R₃, and R₄ are independently organic and/or oligomeric ligands or may be hydrogen.

[0068] Examples of useful organic ligands include, but are not limited to, linear or branched alkyl groups having 1 to 22 carbon atoms, aralkyl groups which are benzyl and substituted benzyl moieties including fused-ring moieties having linear chains or branches of 1 to 100 carbon atoms in the alkyl portion of the structure, aryl groups such as phenyl and substituted phenyl including fused-ring aromatic substituents, beta, gamma unsaturated groups having six or less carbon atoms, and alkyleneoxide groups having repeating units comprising 2 to 6 carbon atoms. Examples of useful oligomeric ligands include, but are not limited to poly(alkylene oxide), polystyrene, polyacrylate, polycaprolactone

[0069] Examples of useful organic cations include, but are not limited to alkyl ammonium ions, such as tetramethyl ammonium, hexyl ammonium, butyl ammonium, bis(2-hydroxyethyl) dimethyl ammonium, hexyl benzyl dimethyl ammonium, benzyl trimethyl ammonium, butyl benzyl dimethyl ammonium, tetrabutyl ammonium, di(2-hydroxyethyl) ammonium, and alkyl phosphonium ions such as tetrabutyl phosphonium, trioctyl octadecyl phosphonium, tetraoctyl phosphonium, octadecyl triphenyl phosphonium, or mixtures thereof.

[0070] Other particularly useful organic cations for this invention include, but are not limited to alkyl ammonium ions such as dodecyl ammonium, octadecyl trimethyl ammonium, bis(2-hydroxyethyl) octadecyl methyl ammonium, octadecyl benzyl dimethyl ammonium, or mixtures thereof.

[0071] Illustrative examples of suitable polyalkoxylated ammonium compounds include the hydrochloride salts of polyalkoxylated amines such as JEFFAMINE (trade name of Huntsman Chemical), namely, JEFFAMINE-506 and JEF-

PAMINE-505, and an amine available under the trade name ETHOMEEN (trade name of Akzo Chemie America), namely, ETHOMEEN 18/25, which is octadecyl bis(polyoxyethylene[15])amine, wherein the numbers in brackets refer to the total number of ethylene oxide units. A further illustrative example of a suitable polyalkoxylated ammonium compound is ETHOQUAD 18/25 (trade name of Akzo Chemie America), which is octadecyl methyl bis(polyoxyethylene [15]) ammonium chloride, wherein the numbers in brackets refer to the total number of ethylene oxide units.

[0072] Numerous methods to modify layered clays with organic cations are known, and any of these may be used in the practice of this invention. One embodiment of this invention is the organic modification of a layered clay with an organic cation salt by the process of dispersing a layered clay or mixture of clays into hot water, most preferably from 50 to 80°C, adding the organic cation salt separately or adding a mixture of the organic cation salts (neat or dissolved in water or alcohol) with agitation, then blending for a period of time sufficient for the organic cations to exchange most of the metal cations present in the galleries between the layers of the clay material(s). Then, the organically modified layered clay material(s) is isolated by methods known in the art including filtration, centrifugation, spray drying, and their combinations.

[0073] It is desirable to use a sufficient amount of the organic cation salt(s) to permit exchange of most of the metal cations in the galleries of the layered particle for the organic cation(s); therefore, at least 0.5 equivalent of total organic cation salt is used and up to 3 equivalents of organic cation salt can be used. It is preferred that 0.5 to 2 equivalents of organic cation salt be used, more preferable 1.0 to 1.5 equivalents. It is desirable, but not required to remove most of the metal cation salt(s) and most of the excess organic cation salt(s) by washing and other techniques known in the art.

20

Other Clay Treatments

[0074] The clay may be further treated for the purposes of aiding exfoliation in the composite and/or improving the strength of the polymer/clay interface. Any treatment that achieves the above goals may be used. Examples of useful treatments include intercalation with water-soluble or water-insoluble polymers, organic reagents or monomers, silane compounds, metals or organometallics, and/or their combinations. Treatment of the clay can be accomplished prior to the addition of a polymer to the clay material, during the dispersion of the clay with the polymer or during a subsequent melt blending or melt fabrication step.

[0075] Examples of useful pretreatment with polymers and oligomers include those disclosed in U.S. Patents 5,552,469 and 5,578,672.

Examples of useful polymers for treating the clay material include polyvinyl pyrrolidone, polyvinyl alcohol, polyethylene glycol, polytetrahydrofuran, polystyrene, polycaprolactone, certain water-dispersible polyesters, Nylon-6.

[0076] Examples of useful pretreatment with organic reagents and monomers include those disclosed in EP 780,340 A1.

[0077] Examples of useful pretreatment with silane compounds include those treatments disclosed in WO 93/11190. Examples of useful silane compounds includes (3-glycidoxypropyl)trimethoxysilane, 2-methoxy (polyethyleneoxy)propyl heptamethyl trisiloxane, octadecyl dimethyl (3-trimethoxysilylpropyl) ammonium chloride.

[0078] If desired, a dispersing aid may be present during or prior to the formation of the composite for the purposes of aiding exfoliation of the treated or untreated swellable layered particles into the polymer. Many such dispersing aids are known and cover a wide range of materials including water, alcohols, ketones, aldehydes, chlorinated solvents, hydrocarbon solvents, aromatic solvents, or combinations thereof.

[0079] It should be appreciated that on a total composition basis, dispersing aids and/or pretreatment compounds may account for significant amount of the total composition, in some cases up to 30 weight percent. While it is preferred to use as little dispersing aid/pretreatment compound as possible, the amounts of dispersing aids and/or pretreatment compounds may be as much as about 8 times the amount of the platelet particles.

50 **Articles**

[0080] The polymer-clay nanocomposite of this invention may be formed into articles by conventional plastic processing techniques. Molded articles may be made from the above-described polymers by compression molding, blow molding, or other such molding techniques, all of which are known in the art. Monolayer and/or multilayer articles prepared from the nanocomposite material of this invention include, but are not limited to film, sheet, pipes, tubes, profiles, molded articles, preforms, stretch blow molded films and containers, injection blow molded containers, extrusion blow molded films and containers, thermoformed articles. The containers are preferably bottles.

[0081] The bottles and containers of this invention provide increased shelf storage life for contents, including bev-

erages and food that are sensitive to the permeation of gases. Articles, more preferably containers, of the present invention often display a gas transmission or permeability rate (oxygen, carbon dioxide, water vapor) of at least 10% lower (depending on clay concentration) than that of similar containers made from clay-free polymer, resulting in correspondingly longer product shelf life provided by the container. Desirable values for the sidewall modulus and tensile strength may also be maintained. The articles also show unexpected resistance to haze formation, crystallization, and other defect formation.

[0082] The articles may also be multilayered. Preferably, the multilayered articles have a nanocomposite material disposed intermediate to other layers, although the nanocomposite may also be one layer of a two-layered article. In embodiments where the nanocomposite and its components are approved for food contact, the nanocomposite may form the food contact layer of the desired articles. In other embodiments, it is preferred that the nanocomposite be in a layer other than the food contact layer.

[0083] The multilayer articles may also contain one or more layers of the nanocomposite composition of this invention and one or more layers of a structural polymer. A wide variety of structural polymers may be used. Illustrative of structural polymers are polyesters, polyetheresters, polyamides, polyesteramides, polyurethanes, polyimides, polyetherimides, polyureas, polyamideimides, polyphenyleneoxides, phenoxy resins, epoxy resins, polyolefins, polyacrylates, polystyrene, polyethylene-co-vinyl alcohols (EVOH), or their combinations and blends. The preferred structural polymers are polyesters, such as poly(ethylene terephthalate) and its copolymers.

[0084] In another embodiment, co-extruding a layer of the polymer-clay nanocomposite specified above with some other suitable thermoplastic resin may form articles. The polymer-clay nanocomposite and the molded article and/or extruded sheet may also be formed at the same time by co-injection molding or co-extruding.

[0085] Another embodiment of this invention is the combined use of silicate layers uniformly dispersed in the matrix of a high barrier thermoplastic together with the multilayer approach to packaging materials. By using a layered clay to decrease the gas permeability in the high barrier layer, the amount of this material that is needed to generate a specific barrier level in the end application is greatly reduced.

[0086] Since the high barrier material is often the most expensive component in multilayer packaging, a reduction in the amount of this material used can be quite beneficial. With the polymer-clay nanocomposite layer being sandwiched between two outer polymer layers, the surface roughness is often considerably less than for a monolayer nanocomposite material. Thus, with a multilayer approach, the level of haze may be further reduced.

30 Processes

[0087] The polymer/clay nanocomposites of this invention may be prepared with the matrix polymer, functionalized oligomer or polymer and layered clay material in different ways.

[0088] In one embodiment of this invention, a polymer or oligomer comprising an ammonium group is prepared. Then, a concentrate is prepared by melt compounding, by methods known in the art, 20-99.5 weight percent, preferably 40-95 weight percent, of the ammonium-functionalized polymer or oligomer with 0.5-80 weight percent, preferably 0.5-60 weight percent, of the desired clay. Then, the final nanocomposite is prepared by melt compounding, by methods known in the art, 1-50 weight percent of the concentrate with 50-99 weight percent of a matrix polymer. The melt compounding steps may be performed separately or sequentially. That is, the concentrate may be either used immediately while in the molten form or may be solidified and used at a later time.

[0089] In another embodiment of this invention, a concentrate of 0.5-80 weight percent of clay intercalated with 20-99.5 weight percent of an ammonium-functionalized polymer or oligomer is prepared in water or a mixture of water and one or more water-miscible organic solvents, including alcohols, ethers, acids, and nitriles. Illustrative of water-miscible organic solvents are dioxane, tetrahydrofuran, methanol, ethanol, isopropanol, acetic acid, acetonitrile, or mixtures thereof. Then, the final nanocomposite is prepared by melt compounding 1-50 weight percent of the concentrate with 50-99 weight percent of a polymer by methods known in the art. The melt compounding steps may be performed separately or sequentially. That is, the concentrate may be either used immediately while in the molten form or may be solidified and used at a later time.

[0090] In another embodiment of this invention, the nanocomposite is prepared in a single extrusion, by methods known in the art, using up to 0.5-25 weight percent of the ammonium-functionalized polymer or oligomer, 50-99 weight percent of the desired polymer, and 0.5-25 weight percent of the desired clay.

[0091] In yet another embodiment of this invention, a polymer is prepared or modified such that a minor amount of the polymer chains comprise an ammonium group. Then, 75-99.5 weight percent of this partially ammonium-functionalized polymer material is melt compounded, by methods known in the art, with 0.5-25 weight percent of the desired clay material.

[0092] In still another embodiment of this invention, an ammonium-functionalized polymer or oligomer is melt blended with a matrix polymer, and then the blend is melt compounded with clay.

[0093] Melt processing or mixing includes melt and extrusion compounding. Use of extrusion compounding to mix

clay and a polymer presents advantages. Chiefly, the extruder is able to handle the high viscosity exhibited by the nanocomposite material. In addition, in a melt mixing approach for producing nanocomposite materials, the use of solvents can be avoided. Low molecular weight liquids can often be costly to remove from the nanocomposite resin.

[0094] A low molecular weight oligomer, for example, is found to be very effective at dispersing an organo or other suitable modified clay, preferably smectic clay, as a concentrate when melt mixed. Desirable values for the I.V. or molecular weight of the functionalized oligomer or polymer depends on factors including the oligomer and clay selected and is readily determined by those skilled in the art.

[0095] If desired, a dispersing aid may be present during or prior to the formation of the composite by melt mixing for the purposes of aiding exfoliation of the treated or untreated swellable layered particles into the polymer. Many such dispersing aids are known covering a wide range of materials including water, alcohols, ketones, aldehydes, chlorinated solvents, hydrocarbon solvents, aromatic solvents, or combinations thereof.

[0096] The molecular weight of the polymer material may be increased by any of a number of known approaches or by any combination of these approaches, e.g., chain extension, reactive extrusion, extrusion let-down, solid state polymerization or annealing, annealing under a flow of inert gas, vacuum annealing, let-down in a melt reactor.

[0097] Although any melt mixing device may be used, typically, melt mixing is conducted either by a batch mixing process or by a melt compounding extrusion process during which treated or untreated layered clay particles are introduced into an oligomeric or polymeric resin. Prior to melt mixing, the treated or untreated layered particles may exist in various forms including pellets, flakes, chips and powder. It is preferred that the treated or untreated layered particles be reduced in size by methods known in the art, such as hammer milling and jet milling. Prior to melt mixing, the oligomeric or polymeric resin may exist in wide variety of forms including pellets, ground chips, powder or its molten state.

[0098] Melt mixing may also be achieved by dry mixing an functionalized oligomeric resin with treated or untreated layered particles then passing the mixture through a compounding extruder under conditions sufficient to melt the oligomeric resin. Further, melt mixing may be conducted by feeding the functionalized oligomeric resin and treated or untreated layered particles separately into a compounding extruder. When treated layered particles are used in this process, it is preferred that the oligomeric resin be added first to minimize degradation of treated layered particles.

[0099] In yet another embodiment involving the melt mixing of a functionalized oligomer, a high concentration of layered particles is melt mixed with oligomeric resin by mixing in a reactor. The resulting composite material is then either chain extended, polymerized to high molecular weight, or let down in the extruder into a high molecular weight polymer to obtain the final nanocomposite material.

[0100] As exemplified above, the clay, the ammonium-functionalized polymer or oligomer, and the matrix polymer components of the nanocomposite of this invention may be combined in a wide variety of ways that are known to those skilled in the art.

[0101] The functionalized oligomer or polymer and the high molecular weight matrix polymer may have the same or different repeat unit structure, i.e., may be comprised of the same or different monomer units. Preferably, the functionalized oligomer or polymer has the same monomer unit to enhance compatibility or miscibility with the high molecular weight matrix polymer.

[0102] The resulting nanocomposite can then be processed into the desired barrier article, film or container with article-forming methods well known in the art. For example, the nanocomposite may then be processed either as an injected molded article, e.g., a container preform or an extruded film or sheet. Additional processing of stretch blow molding to a container or extruding as a barrier film yields transparent high barrier finished articles. Polymer nanocomposites and articles produced according to the present invention display a gas permeability, which is at least 10 percent lower than that of the unmodified polymer.

45 Examples

[0103] The following examples and experimental results are included to provide those of ordinary skill in the art with a complete disclosure and description of particular manners in which the present invention can be practiced and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature) ; however, some errors and deviations may have occurred. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

Example 1

[0104] This example illustrates the preparation of amine functionalized polyesters by aminolysis of an oligomeric poly(caprolactone).

[0105] 200 grams (about 0.1 moles) of polycaprolactone, with number average molecular weight of about 2000 avail-

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able from Aldrich, and 30 grams (0.30 moles) of 2,2-dimethyl-1,3-propanediamine were heated with stirring at 200°C for 90 minutes and at 220°C for 30 minutes in a 500-mL 3-neck round-bottom flask equipped with stirrer, condensor, and nitrogen inlet. The resulting liquid resin was poured into a can. Titration of a small sample indicated that the amine content in the sample is 2.08 meq/g, and molecular weight analysis indicated a significant decrease in molecular weight.

5 20 grams of the product was stirred in 160 ml of 60 °C water, and the ammonium form was prepared by adding 10 meq of hydrochloric acid in 10 ml of water.

[0106] 6.36 g (6.14 meq of exchangeable sodium) of refined Wyoming type sodium montmorillonite with cation exchange capacity of 0.95 meq/g available from Southern Clay Products was dispersed in 500 ml of 70°C water in a Vitamix (trade name) blender. Then 3.07 g (6.14 meq of ammonium) of the ammonium functionalized polycaprolactone in 150 ml of water was added. The mixture was then blended, filtered, washed with 500 ml of water twice in the Vitamix blender, then dried in an oven at 60°C. The volume average particle size of the clay material was reduced to less than 10 microns by hammer milling then jet milling. The resulting concentrate of clay and ammonium functionalized polycaprolactone was determined to have a WAXS basal spacing of 1.4 nm.

15 Example 2

[0107] The procedure of Example 1 was repeated except that, PETG 6763, which is poly(ethylene-co-1,4-cyclohexanedimethylene terephthalate) with IV of 0.75 dL/g available from Eastman Chemical Company, was used instead of polycaprolactone, and the temperature was increased to 225°C.

20 Example 3

[0108] The procedure of Example 2 was repeated except that AQ 55 (trade name), which is a water dispersible melt processible polyester available from Eastman Chemical Company, was used in place of PETG 6763.

25 Example 4

[0109] The procedure of Example 2 was repeated except that oligomeric poly(ethylene adipate) was used in place of polycaprolactone.

30 Examples 5-18

[0110] The above procedure was repeated using the following polyesters and amines in the molar ratio indicated in Table 1 below.

35 Table 1

Ex	Polyester	Amine	Moles of Amine per mole of Polyester	I.V. of Amine Functionalized Polyester (dL/g)	Basal Spacing of Clay Concentrate (nm)
5	PETG 6763	Dimethylethanolamine	0.17	0.10	1.4
6	PETG 6763	Dimethylethanolamine	0.44	0.12	1.4
7	PETG 6763	Dimethylaminopropylamine	0.17	0.28	1.3
8	PETG 6763	Dimethylaminopropylamine	0.44	0.10	1.4
9	AQ 55	Dimethylethanolamine	0.17	0.13	
10	AQ 55	Dimethylethanolamine	0.44	0.08	1.4
11	AQ 55	Dimethylaminopropylamine	0.17	0.23	1.5
12	AQ 55	Dimethylaminopropylamine	0.44	0.11	
13	Polycaprolactone	Dimethylethanolamine	0.17	0.19	1.5
14	Polycaprolactone	Dimethylethanolamine	0.44	0.15	1.4
15	Polycaprolactone	Dimethylaminopropylamine	0.17	0.15	1.8
16	Polycaprolactone	Dimethylaminopropylamine	0.44	0.10	3.3

Table 1 (continued)

Ex	Polyester	Amine	Moles of Amine per mole of Polyester	I.V. of Amine Functionalized Polyester (dL/g)	Basal Spacing of Clay Concentrate (nm)
17	Polyethylene adipate	Dimethylethanolamine	0.50		2.0
18	Polyethylene adipate	Dimethylethanolamine	0.50		2.1

Example 19

[0111] A dimethylamine terminated oligomeric polystyrene was prepared by anionic polymerization of styrene using 3-(dimethylamino)propyl lithium as the initiator using vacuum line conditions with a complex solvent mixture of cyclohexane, benzene, and tetrahydrofuran. The number average molecular weight of the dimethylamine-terminated polystyrene was determined to be about 700 by MALDI-TOF.

[0112] 6.6 grams of the above material was dissolved in 290 ml of dioxane then 10 g of 0.97 N hydrochloric acid was added to give the ammonium form of the oligomeric polystyrene. 10 grams of refined Wyoming type sodium montmorillonite with cation exchange capacity of 0.95 meq/g available from Southern Clay Products was dispersed in a 70°C mixture of 90 ml of water and 110 ml of dioxane in a blender. The solution of the ammonium-functionalized polystyrene was added to the blender. The mixture was then blended, filtered, washed once with dioxane and once with water, then dried in an oven at 60°C. The volume average particle size of the clay material was reduced to less than 10 microns by hammer milling then jet milling. The resulting concentrate of clay and ammonium functionalized polystyrene was determined to have a WAXS basal spacing of 1.8 nm.

Example 20

[0113] The concentrates prepared in Examples 1-19 are dry mixed with PET 9921, dried overnight, then extruded on a Leistritz Micro-18 (trade name) twin-screw extruder at 280°C. The extruded strand is air cooled and chopped into pellets. The pellets are dried in a vacuum oven overnight then extruded into film using a 1-inch Killion single screw extruder with a 10.2 cm (4-inch) film dye. Oxygen permeability measurements of the film on a Mocon Oxtran 1000 (trade name) show a significant reduction compared to film of PET 9921.

Example 21

[0114] A dimethylamine terminated oligomeric polystyrene was prepared by anionic polymerization of styrene using 3-(dimethylamino)propyl lithium as the initiator using vacuum line conditions with a complex solvent mixture of cyclohexane, benzene, and tetrahydrofuran. The number average molecular weight of the dimethylamine-terminated polystyrene was determined to be about 1200 by MALDI-TOF. The dimethylammonium terminated oligomeric polystyrene was prepared by treating the dimethylamine terminated oligomeric polystyrene with 1 equivalent of hydrochloric acid in a mixture of dioxane and water, concentrating the solvent, then precipitating the product by adding a large amount of isopropanol.

[0115] 120 g of the above ammonium functionalized oligomeric polystyrene, 8 g of an octadecyltrimethyl ammonium intercalated montmorillonite with volume average particle size of 10-15 microns from Nanocor, and 872 g of polystyrene, are dry blended, dried in a vacuum oven at 100°C overnight, then extruded on a Leistritz Micro-18 (trade name) twin-screw extruder at 200°C. The extruded strand is air cooled and chopped into pellets.

[0116] 700 g of the above pellets is dried in a vacuum oven overnight at 100°C then extruded into film. Oxygen permeability measurements on a Mocon Oxtran 1000 (trade name) show a significant reduction compared to a clay-free control.

Example 22

[0117] An amine functionalized polyethylene-co-vinyl acetate is prepared using an amine-functionalized initiator. Then, the ammonium functionalized polyethylene-co-vinyl alcohol is prepared by hydrolysis of the amine functionalized polyethylene-co-vinyl acetate.

[0118] 120 g of the above ammonium functionalized polyethylene-co-vinyl alcohol, 7 g of a refined sodium montmo-

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illonite with volume average particle size of 10-15 microns available from Nanocor, and 873 g of Eval F101A, which is a polyethylene-co-vinyl alcohol available from Eval Company U.S.A., are dry blended, dried in a vacuum oven at 100°C overnight, then extruded on a Leistritz Micro-18 twin-screw extruder at 200°C. The extruded strand is air cooled and chopped into pellets.

5 [0119] 700 g of the above pellets is dried in a vacuum oven overnight then extruded into trilayer film with two outside layers of PET-9921. 5.1 cm (2-inch) square samples of the film are oriented 4x4 in a T. M. Long instrument. Oxygen permeability measurements on a Mocon Oxtran 2/20 (trade name) show a significant reduction compared to a clay-free control.

10 Example 23

[0120] An amine functionalized terpolymer comprising 33 mole percent of ethylene, 62 mole percent of vinyl acetate, and 5 mole percent of 6-(N,N-dimethylamino)hexyl vinyl ether is prepared. Then, this material is converted into an ammonium functionalized polyethylene-co-vinyl alcohol by hydrolysis of the terpolymer.

15 [0121] 120 g of the above ammonium functionalized polyethylene-co-vinyl alcohol, 7 g of a refined sodium montmorillonite with volume average particle size of 10-15 microns available from Nanocor, and 873 g of Eval F101A, which is a polyethylene-co-vinyl alcohol available from Eval Company U.S.A., are dry blended, dried in a vacuum oven at 100°C overnight, then extruded on a Leistritz Micro-18 (trade name) twin-screw extruder at 200°C. The extruded strand is air cooled and chopped into pellets.

20 [0122] 700 g of the above pellets is dried in a vacuum oven overnight then extruded into trilayer film with two outside layers of PET-9921. 5.1 cm (2-inch) square samples of the film are oriented 4x4 in a T. M. Long instrument. Oxygen permeability measurements on a Mocon Oxtran 2/20 (trade name) show a significant reduction compared to a clay-free control.

25 Example 24

[0123] An ammonium functionalized poly(meta-xylylene adipamide) is prepared from 6-(trimethylammonium)hexanoic acid, adipic acid, and meta-xylylenediamine. 120 g of the ammonium functionalized poly(meta-xylylene adipamide), 8 g of an octadecylammonium intercalated montmorillonite from Nanocor, Inc., and 872 g of MxD6 6007 polyamide from Mitsubishi Gas, are dry blended, dried in a vacuum oven at 110°C overnight, then extruded on a Leistritz Micro-18 twin-screw extruder at 280°C. The extruded strand is air cooled and chopped into pellets.

30 [0124] 700 g of the above pellets is crystallized then dried in a vacuum oven overnight then extruded into trilayer film with two outside layers of PET-9921. 5.1 cm (2-inch) square samples of the film are oriented 4x4 in a T. M. Long instrument. Oxygen permeability measurements on a Mocon Oxtran 2/20 (trade name) show a significant reduction compared to a clay-free control.

Claims

40 1. A polymer-clay nanocomposite comprising:

(i) a melt-processible matrix polymer,
(ii) a layered clay material, and
(iii) a matrix polymer-compatible oligomer or polymer having an onium functional group bonded thereto,

45 wherein the melt processible matrix polymer has dispersed therein platelet particles derived from components (ii) and (iii).

50 2. A polymer-clay nanocomposite according to claim 1 obtainable by incorporating in the melt-processible matrix polymer a concentrate comprising the layered clay material and the matrix polymer-compatible oligomer or polymer having an onium functional group bonded thereto.

55 3. The nanocomposite of claim 1 or claim 2, wherein the melt-processible matrix polymer comprises a polyester, polyetherester, polyamide, polyesteramide, polyurethane, polyimide, polyetherimide, polyurea, polyamideimide, polyphenyleneoxide, phenoxy resin, epoxy resin, polyolefin, polyacrylate, polystyrene, polyethylene-co-vinyl alcohol, or a copolymer thereof, or a mixture thereof.

4. The nanocomposite of claim 1 or claim 2, wherein the onium functional group is an ammonium group.

5. The nanocomposite of claim 1 or claim 2, wherein the melt-processible matrix polymer comprises a partially aromatic polyamide, aliphatic polyamide, wholly aromatic polyamide or a mixture thereof.
6. The nanocomposite of claim 1 or claim 2, wherein the melt-processible matrix polymer comprises poly(m-xylylene adipamide) or a copolymer thereof, isophthalic acid-modified poly(m-xylylene adipamide), nylon-6, nylon-6,6, or a copolymer thereof, EVOH or a mixture thereof.
- 10 7. The nanocomposite of claim 1 or claim 2, wherein the melt-processible matrix polymer comprises poly(ethylene terephthalate) or a copolymer thereof, or a mixture thereof.
8. The nanocomposite of claim 1 or claim 2, comprising greater than zero to 25 weight percent of the layered clay material.
- 15 9. The nanocomposite of claim 1 or claim 2, comprising from 0.5 to 15 weight percent of the layered clay material.
10. The nanocomposite of claim 1 or claim 2, wherein the layered clay material comprises montmorillonite, hectorite, mica, vermiculite, bentonite, nontronite, beidellite, volkonskoite, saponite, magadite, kenyaita, or a mixture thereof.
- 20 11. The nanocomposite of claim 1 or claim 2, wherein the layered clay material comprises Wyoming-type sodium montmorillonite or Wyoming-type sodium bentonite.
12. The nanocomposite of claim 1 or claim 2, wherein the layered clay material is a free flowing powder having a cation exchange capacity from 0.9 to 1.5 meq/g.
- 25 13. The nanocomposite of claim 1 or claim 2, wherein at least 50 percent of the layered clay material is dispersed in the form of individual platelet particles and tactoids in the matrix polymer and the individual platelet particles have a thickness of less than 2 nm and a diameter of from 10 to 3000 nm.
14. The nanocomposite of claim 1 or claim 2, wherein the oligomer or polymer having an onium functional group bonded thereto and the melt-processible matrix polymer have the same monomer unit.
- 30 15. The nanocomposite of claim 1 or claim 2, wherein the layered clay material is treated with an organic cation.
16. The nanocomposite of claim 15, wherein the organic cation is derived from onium salt compound.
- 35 17. The nanocomposite of claim 16, wherein the onium salt compound comprises an ammonium or phosphonium salt compound.
18. The nanocomposite of claim 16, wherein the organic cation comprises an alkyl ammonium ion, alkyl phosphonium ion, polyalkoxylated ammonium ion, or a mixture thereof.
- 40 19. The nanocomposite of claim 1 or claim 2, wherein the melt-processible matrix polymer comprises poly(ethylene terephthalate) or a copolymer thereof and the layered clay material comprises Wyoming-type sodium montmorillonite or Wyoming-type sodium bentonite.
20. An article prepared from the nanocomposite of claim 1.
21. The article of claim 20 in the form of film, sheet, pipe, an extruded article, a molded article or a molded container.
- 50 22. The article of claim 20 in the form of a bottle.
23. The article of claim 20, wherein the said nanocomposite has a gas permeability which is at least 10 percent lower than that of a clay-free polymer.
- 55 24. An article having a plurality of layers wherein at least one layer is formed from the nanocomposite of claim 1.
25. The article of claim 24, wherein the nanocomposite is disposed intermediate to two other layers.

26. The article of claim 24, having one or more layers of a structural polymer.

27. A process for preparing a polymer-clay nanocomposite comprising: melt mixing a layered clay material, an oligomer or polymer having an onium functional group bonded thereto, and a melt-processible matrix polymer to form a polymer-clay nanocomposite material.

5 28. The process of claim 27, wherein the nanocomposite material comprises from 0.5 to 25 weight percent of the polymer or oligomer having an onium functional group bonded thereto, from 50 to 99 weight percent of the matrix polymer, and from 0.5 to 25 weight percent of the layered clay material.

10 29. The process of claim 27, wherein the onium functional group is an ammonium group.

30. The process of claim 27, comprising the steps of:

15 (i) forming a concentrate comprising the layered clay material and the oligomer or polymer having an onium functional group bonded thereto, and
(ii) melt mixing the concentrate with the melt-processible matrix polymer to form the polymer-clay nanocomposite.

20 31. The process of claim 30, wherein steps (i) and (ii) are conducted by a batch mixing or a melt compounding extrusion process.

32. The process of claim 30, wherein the concentrate is prepared in water or a mixture of water and one or more water-miscible organic solvents comprising alcohols, ethers, acids, and nitriles.

25 33. The process of claim 32, wherein the water-miscible organic solvents comprise dioxane, tetrahydrofuran, methanol, ethanol, isopropanol, acetic acid, acetonitrile, or mixtures thereof.

34. The process of claim 30, wherein the oligomer or polymer having an onium functional group bonded thereto and the melt-processible matrix polymer have the same monomer unit.

30 35. The process of claim 30, wherein the concentrate of step (i) comprises from 20 to 99.5 weight percent of the polymer or oligomer having an onium functional group bonded thereto and from 0.5 to 80 weight percent of the layered clay material.

35 36. The nanocomposite of claim 2, wherein the concentrate of step (i) comprises from 20 to 99.5 weight percent of the polymer or oligomer having an onium functional group bonded thereto and from 0.5 to 80 weight percent of the layered clay material.

40 37. The nanocomposite of claim 1 comprising from 0.5 to 25 weight percent of the polymer or oligomer having an onium functional group bonded thereto, from 50 to 99 weight percent of the matrix polymer, and from 0.5 to 25 weight percent of the layered clay material.

45 Patentansprüche

1. Polymer-Ton-Nanoverbundstoff, umfassend:

50 (i) schmelzverarbeitbares Matrixpolymer,
(ii) Schichttonmaterial und
(iii) Matrixpolymer-kompatibles Oligomer oder Polymer mit einer daran gebundenen funktionellen Oniumgruppe,

55 wobei in dem schmelzverarbeitbaren Matrixpolymer Plättchenpartikel, abgeleitet von den Komponenten (ii) und (iii), dispergiert sind.

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2. Polymer-Ton-Nanoverbundstoff gemäß Anspruch 1, erhältlich durch Einbringen in das schmelzverarbeitbare Matrixpolymer eines Konzentrats, umfassend das Schichttonmaterial und das Matrixpolymer-kompatible Oligomer oder Polymer mit einer daran gebundenen funktionellen Oniumgruppe.
- 5 3. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das schmelzverarbeitbare Matrixpolymer einen Polyester, Polyetherester, Polyamid, Polyesteramid, Polyurethan, Polyimid, Polyetherimid, Polyharnstoff, Polyamidimid, Polyphenylenoxid, Phenoxyharz, Epoxyharz, Polyolefin, Polyacrylat, Polystyrol, Polyethylen-co-vinyl-alkohol oder ein Copolymer davon oder eine Mischung hiervon umfasst.
- 10 4. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei die funktionelle Oniumgruppe eine Ammoniumgruppe ist.
- 15 5. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das schmelzverarbeitbare Matrixpolymer ein teilweise aromatisches Polyamid, aliphatisches Polyamid, vollständig aromatisches Polyamid oder eine Mischung davon umfasst.
- 20 6. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das schmelzverarbeitbare Matrixpolymer Poly(m-xylylenadipamid) oder ein Copolymer davon, Isophthalsäuremodifiziertes Poly(m-xylylenadipamid), Nylon-6, Nylon-6,6 oder ein Copolymer davon, EVOH oder eine Mischung hiervon umfasst.
- 25 7. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das schmelzverarbeitbare Matrixpolymer Poly(ethylenterephthalat) oder ein Copolymer davon oder eine Mischung hiervon umfasst.
8. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, umfassend mehr als null bis 25 Gew.-% des Schichttonmaterials.
- 25 9. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, umfassend 0,5 bis 15 Gew.-% des Schichttonmaterials.
10. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das Schichttonmaterial Montmorillonit, Hectorit, Mica, Vermiculit, Bentonit, Nontronit, Beidellit, Volkonskoit, Saponit, Magadit, Kenyaite oder eine Mischung hiervon umfasst.
- 30 11. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das Schichttonmaterial Natriummontmorillonit vom Wyoming-Typ oder Natriumbentonit vom Wyoming-Typ umfasst.
- 35 12. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das Schichttonmaterial ein frei fließendes Pulver mit einem Kationenaustauschvermögen von 0,9 bis 1,5 mäqu./g ist.
13. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei mindestens 50 Prozent des Schichttonmaterials dispergiert sind in Form einzelner Plättchenpartikel und Takoide in dem Matrixpolymer und die einzelnen Plättchenpartikel eine Dicke von weniger als 2 nm und einen Durchmesser von 10 bis 3000 nm haben.
- 40 14. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das Oligomer oder Polymer mit einer daran gebundenen funktionellen Oniumgruppe und das schmelzverarbeitbare Matrixpolymer dieselbe Monomereinheit besitzen.
15. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das Schichttonmaterial mit einem organischen Kation behandelt wird.
- 50 16. Nanoverbundstoff gemäß Anspruch 15, wobei das organische Kation von einer Oniumsalzverbindung abgeleitet ist.
17. Nanoverbundstoff gemäß Anspruch 16, wobei die Oniumsalzverbindung eine Ammoniumoder Phosphoniumsalzverbindung umfasst.
- 55 18. Nanoverbundstoff gemäß Anspruch 16, wobei das organische Kation ein Alkylammoniumion, Alkylphosphoniumion, polyalkoxyliertes Ammoniumion oder eine Mischung hiervon umfasst.

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19. Nanoverbundstoff gemäß Anspruch 1 oder Anspruch 2, wobei das schmelzverarbeitbare Matrixpolymer Poly(ethylenterephthalat) oder ein Copolymer davon umfasst und das Schichtonmaterial Natriummontmorillonit vom Wyoming-Typ oder Natriumbentonit vom Wyoming-Typ umfasst.
- 5 20. Gegenstand, hergestellt aus dem Nanoverbundstoff nach Anspruch 1.
21. Gegenstand nach Anspruch 20 in der Form einer Feinfolie, Folie bzw. Tafel, eines Schlauchs, eines extrudierten Gegenstands, eines Formarikels oder eines geformten Behälters.
- 10 22. Gegenstand nach Anspruch 20 in der Form einer Flasche.
23. Gegenstand nach Anspruch 20, wobei der Nanoverbundstoff eine Gasdurchlässigkeit besitzt, die mindestens 10 Prozent geringer ist als diejenige eines tonfreien Polymers.
- 15 24. Gegenstand mit einer Vielzahl an Schichten, wobei mindestens eine Schicht aus dem Nanoverbundstoff nach Anspruch 1 gebildet ist.
25. Gegenstand nach Anspruch 24, wobei der Nanoverbundstoff zwischen zwei anderen Schichten angeordnet ist.
- 20 26. Gegenstand nach Anspruch 24, mit einer oder mehreren Schichten aus einem Strukturpolymer.
27. Verfahren zur Herstellung eines Polymer-Ton-Nanoverbundstoffs, umfassend: das Schmelzmischen eines Schichtonmaterials, eines Oligomers oder Polymers mit einer daran gebundenen funktionellen Oniumgruppe und eines schmelzverarbeitbaren Matrixpolymeren zur Bildung eines Polymer-Ton-Nanoverbundstoffmaterials.
- 25 28. Verfahren nach Anspruch 27, wobei das Nanoverbundstoffmaterial 0,5 bis 25 Gew.-% des Polymers oder Oligomers mit einer daran gebundenen funktionellen Oniumgruppe, 50 bis 99 Gew.-% des Matrixpolymers und 0,5 bis 25 Gew.-% des Schichtonmaterials umfasst.
- 30 29. Verfahren nach Anspruch 27, wobei die funktionelle Oniumgruppe eine Ammoniumgruppe ist.
30. Verfahren nach Anspruch 27, umfassend die Schritte:
 - (i) Bilden eines Konzentrats, umfassend das Schichtonmaterial und das Oligomer oder Polymer mit einer daran gebundenen funktionellen Oniumgruppe, und
 - (ii) Schmelzmischen des Konzentrats mit dem schmelzverarbeitbaren Matrixpolymer zur Bildung des Polymer-Ton-Nanoverbundstoffs.
- 40 31. Verfahren nach Anspruch 30, wobei die Schritte (i) und (ii) durch ein satzweises Mischoder Schmelzkompoundierungs-Extrusionsverfahren durchgeführt werden.
32. Verfahren nach Anspruch 30, wobei das Konzentrat in Wasser oder in einer Mischung aus Wasser und einem oder mehreren wassermischbaren organischen Lösungsmitteln, Alkohole, Ether, Säuren und Nitrile umfassend, hergestellt wird
- 45 33. Verfahren nach Anspruch 32, wobei die wassermischbaren organischen Lösungsmittel Dioxan, Tetrahydrofuran, Methanol, Ethanol, Isopropanol, Essigsäure, Acetonitril oder Mischungen davon umfassen.
- 50 34. Verfahren nach Anspruch 30, wobei das Oligomer oder Polymer mit einer daran gebundenen funktionellen Oniumgruppe und das schmelzverarbeitbare Matrixpolymer dieselbe Monomereinheit aufweisen.
35. Verfahren nach Anspruch 30, wobei das Konzentrat von Schritt (i) 20 bis 99,5 Gew.-% des Polymers oder Oligomers mit einer daran gebundenen funktionellen Oniumgruppe und 0,5 bis 80 Gew.-% des Schichtonmaterials umfasst.
- 55 36. Nanoverbundstoff nach Anspruch 2, wobei das Konzentrat von Schritt (i) 20 bis 99,5 Gew.-% des Polymers oder Oligomers mit einer daran gebundenen funktionellen Oniumgruppe und 0,5 bis 80 Gew.-% des Schichtonmaterials umfasst.

37. Nanoverbundstoff nach Anspruch 1, umfassend 0,5 bis 25 Gew.-% des Polymers oder Oligomers mit einer daran gebundenen funktionellen Oniumgruppe, 50 bis 99 Gew.-% des Matrixpolymers und 0,5 bis 25 Gew.-% des Schichttonmaterials.

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Revendications

1. Nanocomposite polymère-argile comprenant :

- 10 (i) un polymère de matrice pouvant être traité à l'état de fusion,
- (ii) un matériau d'argile en couches, et
- (iii) un oligomère ou polymère compatible avec le polymère de matrice ayant un groupe fonctionnel onium lié à celui-ci,

15 dans lequel le polymère de matrice pouvant être traité à l'état de fusion présente des particules de plaquettes dérivées des constituants (ii) et (iii) dispersées dans celui-ci.

2. Nanocomposite polymère-argile selon la revendication 1 pouvant être obtenu en incorporant dans le polymère de matrice pouvant être traité à l'état de fusion un concentré comprenant le matériau d'argile en couches et l'oligomère ou le polymère compatible avec le polymère de matrice ayant un groupe fonctionnel onium lié à celui-ci.

25 3. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le polymère de matrice pouvant être traité à l'état de fusion comprend un polyester, un polyétherester, un polyamide, un polyesteramide, un polyuréthane, un polyimide, un polyétherimide, une polyurée, un polyamideimide, un poly(oxyde de phénylène), une résine phenoxy, une résine époxy, une polyoléfine, un polyacrylate, un polystyrène, un polyéthylène-co-alcool vinylique ou un copolymère de ceux-ci ou un mélange de ceux-ci.

30 4. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le groupe fonctionnel onium est un groupe ammonium.

35 5. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le polymère de matrice pouvant être traité à l'état de fusion comprend un polyamide partiellement aromatique, un polyamide aliphatique, un polyamide totalement aromatique ou un mélange de ceux-ci.

40 6. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le polymère de matrice pouvant être traité à l'état de fusion comprend du poly(m-xylylène adipamide) ou un copolymère de celui-ci, du poly(m-xylylène adipamide) modifié par de l'acide isophthalique, du Nylon-6, du Nylon-6,6 ou un copolymère de ceux-ci, EVOH ou un mélange de ceux-ci.

45 7. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le polymère de matrice pouvant être traité à l'état de fusion comprend du poly(éthylène téréphthalate) ou un copolymère de celui-ci ou un mélange de celui-ci.

8. Nanocomposite selon la revendication 1 ou la revendication 2 comprenant plus de 0 à 25 % en poids du matériau 45 d'argile en couches.

9. Nanocomposite selon la revendication 1 ou la revendication 2 comprenant de 0,5 à 15 % en poids du matériau d'argile en couches.

50 10. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le matériau d'argile en couches comprend de la montmorillonite, de l'hectorite, du mica, de la vermiculite, de la bentonite, de la nontronite, de la bédellite, de la volkonskoïte, de la saponite, de la magadite, de la kenzaïte ou un mélange de celles-ci.

55 11. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le matériau d'argile en couches comprend de la montmorillonite de sodium de type Wyoming ou de la bentonite de sodium de type Wyoming.

12. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le matériau d'argile en couches est une poudre s'écoulant librement ayant une capacité d'échange de cations de 0,9 à 1,5 meq/g.

13. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel au moins 50 % du matériau d'argile en couches sont dispersés dans la forme de particules de plaquettes individuelles et de tactoïdes dans le polymère de matrice et les particules de plaquettes individuelles ont une épaisseur inférieure à 2 nm et un diamètre de 10 à 3 000 nm.

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14. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel l'oligomère ou le polymère ayant un groupe fonctionnel onium lié à celui-ci et le polymère de matrice pouvant être traité à l'état de fusion présentent la même unité monomère.

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15. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le matériau d'argile en couches est traité avec un cation organique.

16. Nanocomposite selon la revendication 15, dans lequel le cation organique est dérivé d'un composé de sel d'onium.

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17. Nanocomposite selon la revendication 16, dans lequel le composé de sel d'onium comprend un composé de sel d'ammonium ou de phosphonium.

18. Nanocomposite selon la revendication 16, dans lequel le cation organique comprend un ion alkylammonium, un ion alkylphosphonium, un ion ammonium polyalcoxylé ou un mélange de ceux-ci.

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19. Nanocomposite selon la revendication 1 ou la revendication 2, dans lequel le polymère de matrice pouvant être traité à l'état de fusion comprend du poly(éthylène téraphthalate) ou un copolymère de celui-ci et le matériau d'argile en couches comprend de la montmorillonite de sodium de type Wyoming ou de la bentonite de sodium de type Wyoming.

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20. Article préparé à partir d'un nanocomposite selon la revendication 1.

21. Article selon la revendication 20 dans la forme de film, de feuille, de tuyau, d'un article extrudé, d'un article moulé ou d'un récipient moulé.

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22. Article selon la revendication 20 dans la forme d'une bouteille.

23. Article selon la revendication 20, dans lequel ledit nanocomposite présente une perméabilité de gaz qui est au moins 10 % inférieure à celle d'un polymère sans argile.

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24. Article ayant plusieurs couches, dans lequel au moins une couche est formée à partir du nanocomposite selon la revendication 1.

25. Article selon la revendication 24, dans lequel le nanocomposite est disposé de manière intermédiaire entre deux autres couches.

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26. Article selon la revendication 24 ayant une ou plusieurs couches d'un polymère structurel.

27. Procédé pour la préparation d'un nanocomposite polymère-argile comprenant : le mélange à l'état de fusion d'un matériau d'argile en couches, d'un oligomère ou polymère ayant un groupe fonctionnel onium lié à celui-ci et d'un polymère de matrice pouvant être traité à l'état de fusion pour former un matériau nanocomposite polymère-argile.

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28. Procédé selon la revendication 27, dans lequel le matériau nanocomposite comprend de 0,5 à 25 % en poids du polymère ou de l'oligomère ayant un groupe fonctionnel onium lié à celui-ci, de 50 à 99 % en poids du polymère de matrice et de 0,5 à 25 % en poids du matériau d'argile en couches.

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29. Procédé selon la revendication 27, dans lequel le groupe fonctionnel onium est un groupe ammonium.

30. Procédé selon la revendication 27 comprenant les étapes consistant :

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(i) à former un concentré comprenant le matériau d'argile en couches et l'oligomère ou polymère ayant un groupe fonctionnel onium lié à celui-ci, et
(ii) à mélanger à l'état de fusion le concentré avec le polymère de matrice pouvant être traité à l'état de fusion

pour former le nanocomposite polymère-argile.

31. Procédé selon la revendication 30, dans lequel les étapes (i) et (ii) sont réalisées par un procédé de mélange discontinu ou de combinaison par extrusion à l'état de fusion.

5 32. Procédé selon la revendication 30, dans lequel le concentré est préparé dans de l'eau ou dans un mélange d'eau et d'un ou plusieurs solvants organiques miscibles à l'eau comprenant des alcools, des éthers, des acides et des nitriles.

10 33. Procédé selon la revendication 32, dans lequel les solvants organiques miscibles à l'eau comprennent le dioxane, le tétrahydrofurane, le méthanol, l'éthanol, l'isopropanol, l'acide acétique, l'acetonitrile ou des mélanges de ceux-ci.

15 34. Procédé selon la revendication 30, dans lequel l'oligomère ou le polymère ayant un groupe fonctionnel onium lié à celui-ci et le polymère de matrice pouvant être traité à l'état de fusion présentent la même unité monomère.

15 35. Procédé selon la revendication 30, dans lequel le concentré de l'étape (i) comprend de 20 à 99,5 % en poids du polymère ou de l'oligomère ayant un groupe fonctionnel onium lié à celui-ci et de 0,5 à 80 % en poids du matériau d'argile en couches.

20 36. Nanocomposite selon la revendication 2, dans lequel le concentré de l'étape (i) comprend de 20 à 99,5 % en poids du polymère ou de l'oligomère ayant un groupe fonctionnel onium lié à celui-ci et de 0,5 à 80 % en poids du matériau d'argile en couches.

25 37. Nanocomposite selon la revendication 1 comprenant de 0,5 à 25 % en poids du polymère ou de l'oligomère ayant un groupe fonctionnel onium lié à celui-ci, de 50 à 99 % en poids du polymère de matrice, et de 0,5 à 25 % en poids du matériau d'argile en couches.

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